

THE TEMPERATURE DEPENDENCE ON THE STRAIN DYNAMICS OF SOLVENT-DILATED COAL

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Key Words: Coal, Viscoelastic, Solvent Swelling

Introduction

The "rubbery" properties of pyridine dilated coals has been recognized for several decades (1). The physical properties of rubbery materials are related to macromolecular structure. For example, measurement of the time-dependent response of a rubber material to applied stresses is one means of obtaining fundamental information on macromolecular structure, such as short range chain flexibility, and long range network topology (2). Previous work exploring the time-dependent compliance of solvent-dilated coals revealed upon the application of a uniaxial compressive stress, numerous coals exhibited both a reversible, viscoelastic strain and an irreversible, viscous strain (3); the irreversible strain was confirmed with creep recovery experiments. This later observation was unexpected as it requires that the coal macromolecule not be covalently cross-linked. It was further noted, however, that the enormity of the viscous coefficients ($\eta \sim 10^{12}$ Poise), coupled with the relatively short time required to reach steady state compliance indicated a structure composed of highly entangled chains with long chain branches. Thus, although the coals are technically not cross-linked, the very small self diffusion coefficients of the entangled macromolecules preclude extraction over reasonable time scales.

In order to characterize the viscoelastic and viscous behavior further, creep compliance experiments have been applied as a function of temperature. By monitoring the temperature dependence on the various dynamic parameters insight can be gained on the molecular scale features that constitute the building blocks of coals macromolecular structure.

Experimental

A sample of the Illinois No. 6 coal, PSOC 1539 was selected for study. This coal is characterized with 81.9 % C, 5.5 % H, 9.4 % O, 1.4 % N, and 2.2 % S. Sections of vitrain (over 95 % vitrinite) were identified and separated from larger blocks with a wafer saw. Small rectangular blocks were sectioned with dimension on the order of 1 x 2 x 2 mm. The blocks were exhaustively extracted in pyridine prior to analysis. Uniaxial stress ($\sim 0.5 \text{ Kg/cm}^2$) was applied to the sample, strain was measured using a microdilatometer employing a linearly variable differential transformer (LVDT). Details on measuring apparatus have been published previously (4). To control temperature, the entire sample holder was placed within a reservoir of pyridine, which was surrounded by an oil bath. Heating tape and a temperature controller were used to establish the temperatures of interest; 25, 50, and 76° C, in this case. During the experiment the inner bath temperature was monitored with a thermocouple; details on the measuring protocol for the variable temperature experiments have been published elsewhere (5).

Results

Figure 1 presents data from a typical creep compliance run. Following the application of uniaxial compressive stress, the swollen coal exhibits a rapid, essentially instantaneous, initial compliance. This evolves into a more gradual viscoelastic compliance spanning several tens of minutes. After approximately 40 minutes the system has reached steady state viscous flow characterized by a constant strain rate. The strain in this during time is totally irreversible. Previous creep experiments were monitored for up to 72 hours. The present experiments were run only long enough to establish steady state deformation.

In general, creep compliance data can be decomposed as the sum of three independent strain components, e.g.

$$J(t) = \frac{t}{\eta} + J_i + \sum_{i=1} J_a(1 - e^{-t/\tau}) \quad (1)$$

Where the first term corresponds to viscous strain, governed by the coefficient of viscosity, η ; the second term corresponds to instantaneous compliance, i.e. very high frequency or glassy strain; the third term corresponds to viscoelastic strain in the so-called "transition

zone", i.e., in the frequency range spanning the "glass transition" (2). This final term is expressed as a sum of exponentially relaxing strain elements. In reality, it would be more appropriate to consider a continuous spectrum of relaxation times as opposed to this discrete representation, e.g.

$$\int_0^{\infty} J(\tau_n)(1 - e^{-t/\tau_n})d\tau \quad (2)$$

The creep compliance, $J(t)$, can be separated into purely viscoelastic and viscous contributions using equation 1, given data that is acquired over a sufficiently long interval of time. Figure 2 presents the purely viscoelastic strain at $T = 25, 50$, and 76°C . The data are normalized to magnitude of the final steady state reversible compliance.

$$\alpha(t)/\alpha_f; \alpha(t) = \Delta L(t)/L; \alpha_f = \Delta L_f/L \quad (3)$$

Each curve is best described by a multiexponential "spectrum" of viscoelastic elements (equation 1 or 2). Significant shifts in the relaxation "spectra" with temperature are clearly evident. One question that arises is whether the different viscoelastic strain elements have the same temperature dependence. For example, a simple chain may exhibit Rouse-like (2) dynamics, where backbone vibrations all contribute to the viscoelastic response. In this case the viscoelastic spectrum is given as proportional to the normal mode frequencies of the coupled oscillators that constitute the simple polymer chain. Of course the temperature dependence of the viscoelastic elements across the frequency spectrum will be the same in such a system. As a consequence of such behavior, each creep compliance curve will be self-similar, when scaled by a time-temperature shift factor a_T^{-1} (6). Indeed, many simple polymers exhibit such behavior.

To test if such behavior is exhibited by the Illinois No. 6 Coal we attempt to scale each curve to match the $T = 76^\circ\text{C}$ viscoelastic curve. We plot the natural log of the shift factors, a_T^{-1} , obtained for the time it takes to reach 50 % and 80 % of the steady state compliance. These are plotted against, $1/T$ (K), in figure 3. If all of the strain viscoelastic strain elements shared the same temperature dependence, then $\ln(a_T^{-1})$ vs $1/T$ for 50% should equal that for 80%. The fact that they do not equate, reveals that viscoelastic elements in different frequency regimes exhibit different temperature dependences. Clearly, the lower frequency modes exhibit a stronger temperature dependence than the higher frequency modes.

This type of behavior has been observed in the case of polymers with side chains, e.g. poly[ethylmethacrylate]. The favored interpretation is that the side chain motion dominates the high frequency, "glassy", deformation, while chain backbone motions dominate the lower frequency, "transition zone", deformation. One can only speculate as to the molecular origin of such variations in the temperature dependence of the viscoelastic properties of solvent dilated coals. It is likely that in place of side chains, oscillations of phenyl groups along the molecular chains within coal may contribute to the high frequency deformation. The lower frequency backbone motion, including the coupled motion of the "virtual" bonds that span the phenyl groups, contributes to the stronger temperature dependence of strain at longer times. This simple picture is complicated, however, by additional factors as described in the discussion section below.

In consideration of the temperature dependence on the viscous deformation it is generally noted that viscous strain (terminal relaxation) follows Arrhenius type behavior, with the temperature dependence being governed by an apparent activation energy given by

$$\eta \propto e^{E_a/RT}$$

Figure 4 presents the viscous coefficients, η , plotted as the natural log of η against $1/T$ (K). Apparent Arrhenius behavior is observed yielding an apparent activation energy of 6.9 Kcal/mol. This value is similar to that of high molecular weight polymer melts and solutions. In general the magnitude of the viscous coefficient in polymeric systems is considered to be related to a molecular friction coefficient (2). Reduction in the molecular friction coefficient with increases in temperature is classically interpreted to be the result of an increase in "free volume" within the system. The viscous data is therefore interpreted to indicate that there is a small positive coefficient of expansion for this solvent dilated coal.

Discussion

At the molecular level, the exact nature of creep in solvent dilated polymers is complex. In general there are two different moduli (both time dependent) that warrant consideration. It is important to recognize the the swelling equilibrium is a balance between

the osmotic stress given by mixing component of the chemical potential and the elastic "pressure" given by the elastic component of the chemical potential (6). Stress applied to one surface of the sample will act with the elastic "pressure" to oppose the osmotic stress leading to compression of the swollen gel through the expulsion of solvent. Calculation of the pure osmotic compressibility for a sample with the dimensions described above, an equilibrium swelling value of $v_2 = 0.42$, and subjected to a uniaxial stress of 0.5 Kg/cm^2 indicates that up to 22 % of the elastic/viscoelastic compliance may be the result of osmotic deswelling.

The osmotic deswelling is clearly time-dependent, subject to requirement that the solvent diffuse out of the network to restore "swelling" equilibrium. The small osmotic strain component corresponds to a 1.4 mol% reduction (calculated) in pyridine. Given that rate of diffusion will be proportional to the chemical potential gradient of solvent inside and out of the network, it is clear that the osmotic deswelling contributes only to the low frequency strain behavior. It is quite possible that the rate of osmotic deswelling is so slow as to be buried within the viscous strain. For example, De-swelling kinetics experiments on similarly sized samples required many hours for full solvent expulsion (7). Additional experiments will need to be run to fully account for the time dependences of the various strain mechanisms. It is clear, however, that the temperature dependence of viscoelastic strain in solvent dilated coals is complex, hence may be some value in characterizing the macromolecular structure of coals.

References

- 1) van Krevelan, Coal, Elsevier Scientific, New York, 1981.
- 2) Ferry, J. D., The Viscoelastic Properties of Polymers; John Wiley & Sons, New York, 1980.
- 3) Cody, G. D., Davis, A., Hatcher, P. G., Energy & Fuels, 7, 455-462
- 4) Cody, G. D., Davis, A., Hatcher, P. G., Energy & Fuels, 1993, 7, 463-468.
- 5) Cody, G. D., Eser, S., Hatcher, P.G., Davis, A., Sobkowiak, M., Shenoy, S., Painter, P. C. Energy & Fuels, 1992, 6, 716
- 6) Flory, P.J., Rehner, J. Chem. Phys., 1944, 12, 412.
- 7) Lei, H., Cody, G. D., French, D. C., Botto, R. E., Hatcher, P. G, Energy & Fuels, 1995, 9, 84

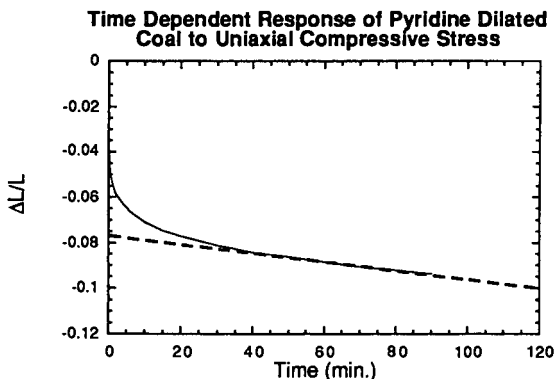


Figure 1: Time dependent Compliance of Solvent Dilated Illinois No. 6 Coal following application of uniaxial compressive stress ($\sim 0.5 \text{ Kg/cm}^2$). Rapid (high frequency) elastic strain grades into viscoelastic (Transition zone) strain, followed by purely viscous (terminal zone) strain. The viscous strain is irreversible.

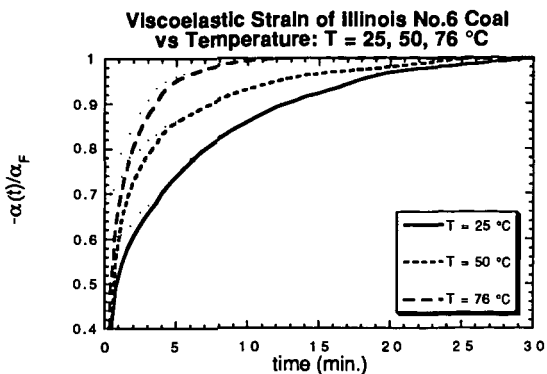


Figure 2: Purely viscoelastic strain (scaled). Temperatures are 25, 50, 76°C. Large shifts towards the higher frequency strain components is clearly evident.

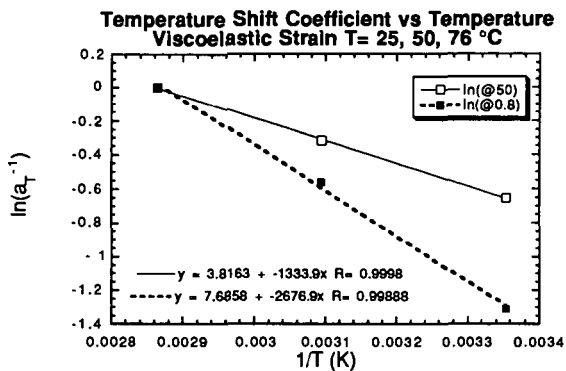


Figure 3: The temperature dependence of the inverse time-temperature shift factor, a_T^{-1} . The different slopes at different extents of total viscoelastic strain reveal that the viscoelastic deformation is not self-similar at different temperatures. The lower frequency modes clearly, exhibit a stronger temperature dependence than the higher frequency modes. This may indicate that different structural elements are dominating different regions of frequency response.

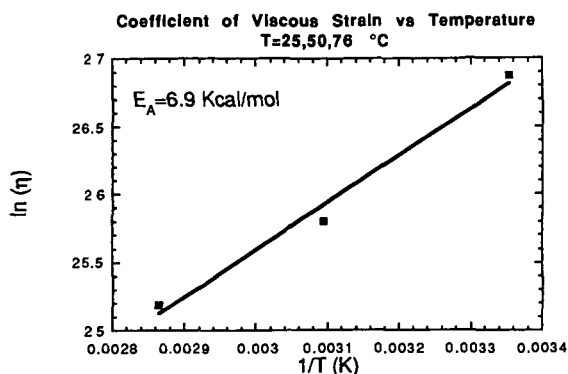


Figure 4: The inverse temperature dependence of the viscous coefficient. The viscosity of polymer/macromolecular melts and solutions typically exhibit Arrhenius type temperature dependences described by an apparent activation energy, E_A . The magnitude of E_A is similar to that of high molecular weight polymer melts, e.g. polyethylene. The positive slope is generally considered to indicate a reduction in the molecular friction factor through a temperature dependent increase in the free volume of the system.